

The Adhesion, Mechanical Properties and Water Resistance of Vinyl Acetate Copolymer Based Blends

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The possibility to use water based vinyl acetate/butyl acrylate (VA/BA) copolymer blends with various content of vinyl ester of versate acid/methyl methacrylate (Veova-10/MMA) or versate acid ester/methyl methacrylate/2-ethylhexylacrylate (Veova-10/MMA/2-EHA) terpolymer for the preparation of adhesive joints after adhesive layer heat reactivation have been investigated. The adhesion, mechanical and physical properties of both pure components and blends have been determined.

The effective enhancement of adhesion properties was obtained when Veova-10/MMA copolymer as modifier was used. After heat reactivation, blends with 20 – 30 wt.% of this modifier show more than 40 % higher peel strength compare to those of non reactivated. The heat treatment results in the increase of tensile strength of free adhesive films. Especially that is expressed for blends with Veova-10/MMA/2-EHA terpolymer. Both the blending and the heat treatment decrease deformability of VA/BA films, also. The influence of modifier type on the films deformability is negligible.

Besides, heat treatment and the increase of polymer modifier content decrease water sorption capability.

Keywords: polymer blends, adhesion, copolymer, strength, water absorption.

INTRODUCTION

For many years, the poly (vinyl acetate) (PVAc) emulsions prepared by the method of emulsion polymerisation are widely used in adhesives, paints, textile finishes, coatings production and so on [1 – 3]. The adhesive industry is one of the most important applications for PVAc emulsion. It has many advantages as an adhesive, e.g. low cost, ease to use and simplicity of application and minimal harmful environment effects. However, there are some inherent disadvantages of PVAc emulsions, which limit their usage.

Usually, such emulsions consist of protective colloids or emulsifiers, which increase the shear strength of adhesive joints, but decrease their water resistance because of the introduction of hydrophilic hydroxy groups into the system [4]. Undesired whitening of the adhesive or a loss of adhesive strength may be the consequence [2 – 8]. In addition, the use of plasticizers to lower the value of minimal film formation temperature and glass transition temperature, while increasing the flexibility of polymer molecules also leads to the reduction of creep resistance and cohesive strength of the adhesive film [9].

One more disadvantage of water-based emulsions usage is long time duration (5 – 7 days) up to full film forming and complete transmission of disperse medium through substrate pores. The suitable way for reduction of film forming duration is evaporation of disperse medium and heat reactivation of adhesive layer before substrates joining at selected conditions [10]. That involves to use water based emulsions for bonding non-porous substrates, also. However, usage of PVAc is limited due to low auto adhesion after its heat reactivation.

PVAc is not generally used as a primary fastener where high strength is needed. Alternative systems, such as vinyl acetate copolymers with various monomers (hydroxy ethyl acrylate, *n*-methynol acrylamide, *n*-isobutoxy methyl acrylamide, etc.) limit the growth of PVAc in specific applications, requiring moderate such properties as water resistance, flexibility or specific adhesion to non-porous surfaces [3, 11]. The ultimate choice is dependent upon the specific product performance requirements. Adhesion often is the primary factor to choose a vinyl acetate copolymer as adhesive.

Vinyl acetate copolymer emulsions with high acrylate content are growing in use as pressure sensitive adhesives for packing and tape applications. Another class utilising butyl and methyl acrylate esters are beginning to merge as laminating adhesives.

The recent investigations were focused on the improvement of the adhesion properties of various modifications of vinyl acetate/butyl acrylate (VA/BA) copolymers by to non-porous substrates comparing their water resistance and mechanical behaviour.

EXPERIMENTAL

All investigated materials were provided by AG “Achema” (Lithuania).

Water - based vinyl acetate/butyl acrylate (VA/BA = 70/30 wt.%) copolymer was used for investigations as the main film forming material.

The copolymers of vinyl ester of versate acid Veova-10 ((R₁)(R₂)C(R₃)–CO–CH=CH₂) were selected for modification VA/BA properties, i.e.:

- vinyl ester of versate acid /methyl methacrylate (Veova-10 /MMA = 70/30 wt.%) copolymer;
- vinyl ester of versate acid /methyl methacrylate /2-ethylhexylacrylate (Veova-10/MMA/2-EHA = 60/30/10 wt.%) terpolymer.

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Poly (vinyl acetate) PVAc emulsion plasticised with 10 wt.% of dibutylphthalate (DF 51/10) was used as control material.

Polymer blends were prepared by mixing selected constituents at high rotational speed ($\omega=2800\text{ s}^{-1}$) for 5 min in ambient atmosphere.

The adhesive properties were evaluated according to the results of T-peel tests of adhesive joints. As substrates textile strips with working area of $S=140\text{ mm}^2$ were used. The adhesive joints were prepared according to two modes:

I mode. The pure polymers or their blends were applied to the textile substrate with a brush and immediately joined together under a pressure of $p=0.25\text{ MPa}$, and pressing duration $\tau_p=30\text{ s}$. The obtained adhesive joints were left to dry for 8 days up to full water elimination through substrate pores and adhesive film formation. After that they were tested.

II mode. Substrates after adhesive layer bonding were left to dry separately up to full water elimination. The duration of open time was 8 days. After that textile strip test pieces were reactivated by the heat in the IR ray field for 60 s and temperature $T=100\text{ }^\circ\text{C}$ in order to obtain viscoelastic state of adhesive layer and in this way to increase autoadhesion of separate layers. After that the pieces immediately joined under pressing conditions, which were the same as in the first adhesive joints preparation mode. The obtained samples were tested after 24 hours. The result was the average value of six samples.

The film samples were casted from the pure emulsions or their blends on the fluoroplastic surface. The water was completely eliminated by slow enough heat treatment at a total duration reaching up to 14 days. The thickness of dried films varied in the range of $600 \div 800\text{ }\mu\text{m}$.

For the tensile measurements the dumbbell shaped specimens with centre zone of 100 mm^2 were prepared. In order to determine the influence of heat reactivation, specimen's before tensile tests were thermally treated for $\tau=1\text{ h}$ at the $T=100\text{ }^\circ\text{C}$. Six specimens were tested for each blend sample.

Mechanical measurements and T-peel tests were carried out on the tensile testing machine FP10/1 at the cross head speed of 0.1 m/min .

The water absorption of dried films was evaluated according to mass changes of samples after their immersion in the distilled water for 24 hours under ambient conditions. The samples were $20 \times 20\text{ mm}^2$ in size. The water absorption capability I during the test was calculated according to formula:

$$I = \frac{M_2 - M_1}{M_1} \times 100\%; \quad (1)$$

where M_1 and M_2 are mass of the test sample before and after its immersing in water for 24 hours, respectively.

RESULTS AND DISCUSSION

The influence of the content of VeoVA-10 copolymers and adhesive joints preparation mode on the adhesion properties of VA/BA copolymer is presented in Fig. 1. It seems that strength of adhesive joints, obtained immediately after adhesive bonding (Fig. 1, a), varies

non-monotonously when polymer modifier content increases. Up to 25 wt.% of modifiers increase the adhesive joint strength: it increases up to $\sim 42\%$ and 25% when modifier VeoVa-10/MMA and VeoVa-10/MMA/2-EHA are used, respectively. However, higher content ($> 25\text{ wt.}\%$) of polymer modifiers results on the decrease of the peel strength.

There are two possible reasons for the perfection of blends adhesion properties in the region of low content of modifiers. Firstly it can be referred to the mutual dissolving of polymers [12]. The other possible factor is based on the formation of reinforcing network structure, similar to a coagulation structure [11]. From the thermodynamical viewpoint, it leads to the increase of cohesive energy of the main matrix (in this case of VA/BA copolymer) and results on the increase of adhesion work.

In order to investigate the possibility to use VA/BA copolymer or its blends with VeoVa-10 derivatives as adhesive for non-porous substrates bonding strength of adhesive joints obtained according to the *II mode*, e.g. after full water elimination in open conditions and adhesive layer reactivation by heating has been evaluated. The obtained results indicate (Fig. 1, b) the increase of cohesion of pure VA/BA copolymer. Peel strength of adhesive joints for pure VA/BA copolymer compared with those obtained without film drying and heat reactivation increases more than 40% (from 2.0 kN/m up to 2.9 kN/m). In this case the effect of the blending depends on the modifier type and its content. The higher intensity of changes was observed when VeoVa-10/MMA bipolymer was used. The 25 wt.% of this modifier increases peel strength of adhesive joints up to 24% , compared with those of unmodified. Meanwhile, influence of VeoVa-10/MMA/2-EHA terpolymer on the adhesive properties changes is negligible, i.e. the amount up to 25 wt.% practically does not influence on the adhesion properties and varies in the range of $2.9 \pm 0.1\text{ kN/m}$. For the blends with higher polymer modifier content ($> 25\text{ wt.}\%$) peel test shows gradual decrease of blends cohesion.

So, the heat reactivation of different modifications of VA/BA blends with VeoVa-10 copolymers or terpolymers are favourable compared with those obtained for adhesive joints without treatment. Obtained results are favourable compare with those for typical PVAc emulsion (Table 1), also. It seems, that reactivation results only in the decrease of peel strength of PVAc down to 55% .

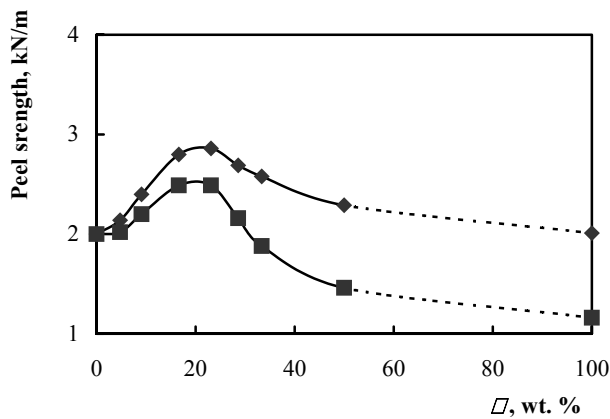
It is possible that during heat reactivation VA/BA copolymer or its blends chains form links and when cools down new links can form between the chains and results on high strength bond between both components and substrate [2]. Meanwhile, for pure PVAc decrease of peel strength after reactivation can be attributed to the degradation processes of internal structure [6].

The mechanical properties of the VA/BA copolymer films and polymer blends are presented in Fig. 2. The tensile strength (Fig. 2, a) of heat treated and untreated VA/BA films are 2.5 and 0.96 MPa , respectively. It indicates that relatively simple procedure of the heat treatment was successful. These results indicate also, that blending of VA/BA with VeoVa-10/MMA/2-EHA or

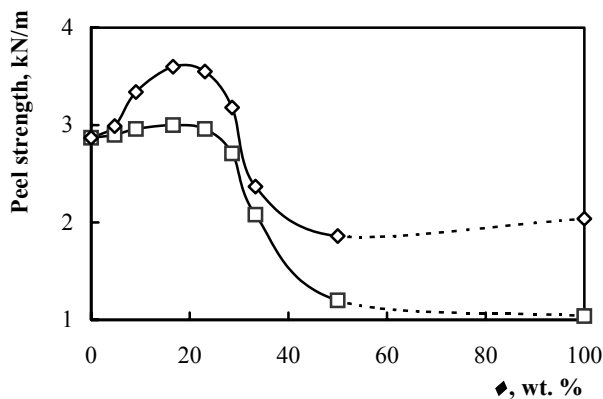
Veova-10/MMA polymers can increase strength of adhesive films. The most remarkable changes were obtained at low content (5 wt.%) of polymer modifiers. The blending results on the monotonous decrease of tensile strength values when modifier content is higher than 5 wt.%. The intensities of changes are related to the heat treatment and modifier type. The blends with Veova-10/MMA/2-EHA terpolymer after heat treatment shows twice higher tensile strength compare to those without heat treatment, and more than eight fold compared to that of pure untreated VA/BA. The influence of this modifier content on the strength variability is negligible. The strength at break decreases only in 6 % (from 6.02 MPa down to 5.72 MPa), when copolymer content increases from 5 wt.% up to 35 wt.%.

Table 1. The properties of PVAc

Property	Treatment type	
	untreated	heat treated
Peel strength P , kN/m	3.42	1.86
Tensile strength σ , MPa	4.71	10.2
Elongation at break ε , %	340	252
Water absorption I , %	16.6	30.8



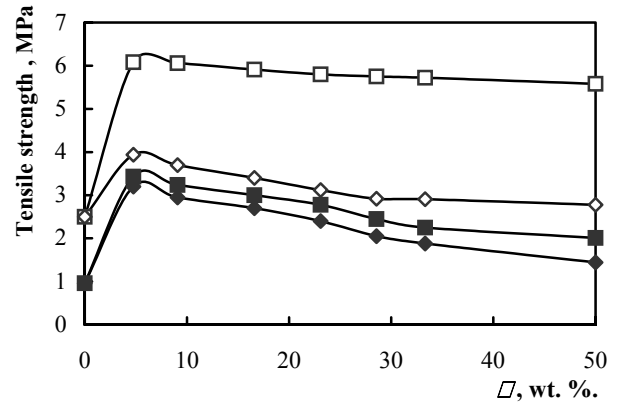
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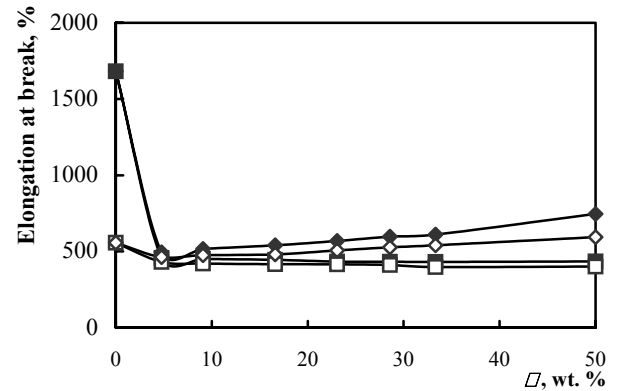
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Fig. 1. The dependence between adhesion properties of VA/BA copolymer and polymer modifier type (◆, ◇ – Veova-10/MMA; ■, □ – Veova-10/MMA/2-EHA), its content φ , and adhesive joints preparation method (a – according to *I mode*, b – according to *II mode*)

The heat treatment for blends, in which Veova-10/MMA copolymer as modifier was used, is less effective. After thermal treatment blends with $\varphi=5$ wt.% of this copolymer shows only 10% enhancement of tensile strength. Besides, the increase of the modifier content results only on the monotonous film weakening. The increase of modifier content from the 5 wt.% to 35 wt.% decreases strength at break down to 30 %.



a



b

Fig. 2. The effect of heat treatment, modifier type and content φ on the tensile strength (a) and elongation (b) at break of VA/BA films (marked as in Fig. 1)

As presented in Table 1 heat treatment is effective tool for enhancement of PVAc films tensile strength, also. Furthermore, the obtained values are higher, than those for VA/BA and its blends.

The effect of blend composition and heat treatment on the free films deformability are presented in Fig. 2, b. It is evident that blending decreases deformability of untreated VA/BA films. The addition of 5 wt.% of the polymer modifier three fold decreases deformation values. In this case elongation at break decreases from 1682 % down to 457 % and 493 % for blends with Veova-10/MMA/2-EHA and Veova-10/MMA, respectively. However, further increase of terpolymer Veova-10/MMA/2-EHA content practically does not effect on the VA/BA films deformability. Only in the case of Veova-10/MMA and VA/BA blends the slight increase of elongation with increase of modifier content was observed. The same dependence for heat treated films is shown, with the exception of the fact that the ε values are 30–50 % smaller compared to those of untreated. More significant

influence of heat treatment and the three fold decrease of elongation at break was found for pure VA/BA. For comparison, deformability of PVAc films after heating diminishes only on the one third.

The obtained effect is probably caused by the increase in VA/BA copolymer ductility after both blending and heat treatment. This speculation is confirmed by the observed means of elongation at break. However, in this case more significant effect of blending was found and influence of the heat treatment on the blends deformability was non significant.

The changes of VA/BA copolymers water absorption ability after blending and heat treatment are presented in Fig. 3. It seems that for non-heated blends water absorption values were found to rise to the maximum as the modifier content increases up to 25 wt.%. Hereafter, it slightly decreases with subsequent increase the modifier content. In this case blends show 3 ÷ 5.5 times higher water absorption values than those obtained from pure components. Unfortunately, they are higher than those for typical PVAc (Table 1).

Quite different water absorption behaviour was obtained after films heating. The increase of terpolymer VeoVa-10/MMA/2-EHA content results on monotonous decrease of water absorption capability. In that time potentiality to water absorption was not clear dependent function of VeoVa-10/MMA copolymer content and varied in the range of 17.2 – 25.3 %.

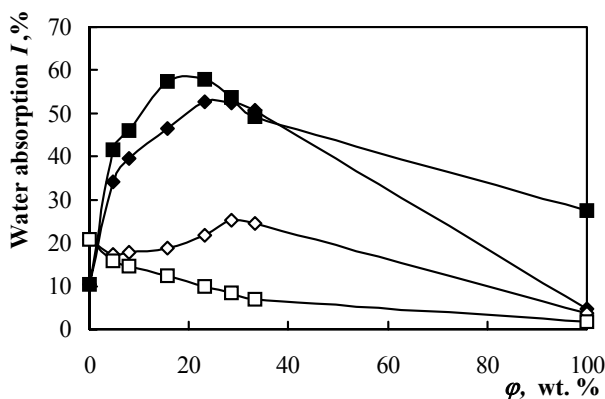


Fig. 3. Water absorption I , % of VA/BA copolymer films versus the modifier type, its content ϕ and heat treatment (marked as in Fig. 1)

It is possible that water absorption phenomenon can be affected by morphological changes such as molecular ordering, chain orientation, intermolecular packing and microvoids. The results suggest that nonheated blends can show poor ordered structure and loose of intermolecular interaction which result in the fast diffusion and high water uptake, while thermal treatment results on the structure ordering and slow water diffusion and decrease of water uptake [9]. Besides, the pure modifiers shows only negligible mass changes after its immersion in water for 24 hours: 3.54 and 1.81 % for VeoVa-10/MMA and for VeoVa-10/MMA/2-EHA, respectively. Whereas, for the pure VA/BA water absorption capability after heat treatment increases twice. The same effect was found for PVAc, as well.

CONCLUSIONS

The possibility to use VA/BA copolymers and its compositions with VeoVa-10/MMA copolymer and VeoVa-10/MMA/2-EHA terpolymer for the preparation of adhesive joints with non-porous substrates, i.e. with full water elimination in open conditions and adhesive layer heat reactivation has been investigated.

The blending with effective amounts of the modifiers (up to 25 wt.%) and heat reactivation is effective tool to enhance cohesion of VA/BA copolymer. Intensity of changes depends on modifier type and content. More effective modifier was found to be VeoVa-10/MMA copolymer, which enhance peel strength more than 40%. On the other hand, incorporation of VeoVa-10/MMA/2-EHA terpolymer and heat treatment improve tensile strength of adhesive films. However, deformability of VA/BA is significantly reduced after both the addition of polymers modifiers and heat treatment.

The heat treatment is effective mean to decrease water absorption capability of polymer blends, but does not effective for pure VA/BA and PVAc.

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